Abstracts and papers submitted to the Meeting of the Nordic Society for Radiation Research and Radiation Technology at the Technical University of Denmark and the Danish Atomic Energy Commission Research Establishment Risø 8th and 9th February 1971

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CHEMISTRY DEPARTMENT

Abstracts and Papers Submitted to the Meeting of the

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at the

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and the

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Telephone: (03) 35 51 01, telex: 5072

A. E. K. Risø

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Risø - M - 1332

Title and author(s)

Abstracts and Papers Submitted to the Meeting of the Nordic Society for Radiation Research and Radiation Technology at the Technical University of Denmark and the Danish Atomic Energy Commission Research Establishment Risö, 8th and 9th February, 1971.

P. Pagsberg

Date January 1971

Department or group

Chemistry Department

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pages + tables + illustrations

Abstract

The abstracts and submitted papers are concerned with a wide variety of subjects within fundamental radiation chemistry and physics, and radiation technology, e.g. γ-radiolysis and pulse radiolysis, hot atom chemistry, positron annihilation, ion implantation, radiation biochemistry and biology, sterilization, dosimetry, experimental instrumentation and data processing, industrial technic and instrumentation.

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A = γ-radiolysis/photochemistry
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C = inorganic systems
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E = biochemistry
F = biology
G = food sterilization
H = stabilized radicals
I = excess electrons
J = positron annihilation
K = ion implantation
L = hot atom chemistry
M = radiation induced polymerization
N = dosimetry
O = data processing
P = instrumentation and technik

Ionization and Properties of the Free Electron in Non Polar Liquids

A.O. Allen, Brookhaven National Laboratory

Recent experiments are reviewed on the processes of ionization and the properties of electrons in non-polar liquids, expecially saturated hydrocarbons. The effects seen in such simple systems as liquid argon are compared with effects in ordinary liquids composed of polyatomic molecules. Electronic properties of branched paraffins differ to an extraordinary extent from those of the straight-chain isomers. Many of these differences depend upon differing mean free paths of electrons in their motions through the medium, which depend in turn on the distribution regions of higher or lower electrostatic potential. A qualitative discussion will be given of potentials in liquid paraffins.

Studies on the Preparation of ionexchange membranes by radiation induced graft copolymerization techniques.

Ismail Aly, Peter Bo
Danish A.E.C. Research Establishment Risø, Denmark

The radiation induced graft copolymerization of mixtures of ethylenesulfonic acid and acrylic acid in their acid-form as well as in the form of their Na-salts on polyethylene films has been studied.

The influence of water and different organic solvents on the grafting efficiency will be discussed.

The simultaneous irradiation method as well as the pre-irradiation technique have been applied.

The exchange capacity for strong and weak acid in the membranes is reported.

Presentation by T. Andersen.

Radiation and ^{32}P-Recoil Reactions in Oxygen Doped KCl-Single Crystals.

by

T. Andersen and J.L. Baptista

Institute of Chemistry

University of Aarhus

Denmark

Doping of pure KCl with oxygen in a closed system leads to formation of a new oxygen-containing centre. Absorption, fluorescence, and ESR spectroscopy have been used together with chemical analysis to characterise the centre, which is suggested to be an O_2^{2-}-anion vacancy association. The radiolysis of the doped KCl-single crystals and the influence of subsequent annealing treatments have been investigated.

The behaviour of ^{32}P-recoil during thermal and photoannealing have been compared in pure and oxygen doped KCl single crystals using reactor irradiation to generate the radiophosphorus. The existence of a new type of ^{32}P(1)-precursor is shown to be responsible for thermal annealing below 140^{0}C in oxygen doped crystals. The new P(1)-precurscr is also present in pure KCl after F-centre bleaching. The radiolysis products of the oxygen dopant and of the host lattice are observed to determine the variation in the valence distribution of ^{32}P.

Presentation by A. Ebbesen.

Chemical Effects of $^{32}P^{+}$-Ions Implanted in NaCl Single Crystals.

by

T. Andersen and A. Ebbesen

Institute of Chemistry

University of Aarhus

Denmark

An electromagnetic isotope separator has been used for the study of the chemical fate of energetic, singly charged ^{32}P ions implanted in NaCl-single crystals. Energetic ^{32}P ions may be able to simulate ^{32}P recoil atoms produced by the $^{35}Cl\ (n,\alpha)\ ^{32}P$ reaction and give new information about the chemical effects following nuclear transformations.

A new chemical sectioning technique has been used to determine the range distribution of the implanted ions as well as changes in the range distribution during subsequent annealing treatments. The chemical distribution of the ^{32}P-atoms was analyzed after dissolution.

A close correspondence between the chemical behaviour of the implanted ions and the range distribution is established. Changes in the chemical distribution of the ^{32}P-atoms during thermal and photoannealing indicate, that centres generated during the slowing down process of the implanted ions play an important role for the chemical valence distribution of the radioactive atoms. The chemical form of the ^{32}P-atoms within the crystal will be discussed.

THE KJELLER GAMMA IRRADIATION PLANT

Ulf Been and Nils Kaltenborn

ABSTRACT

In 1970 a new gamma irradiation facility was taken into use for radiation research and technology in Norway. The discontinuation of the JEEP I reactor operation made available at Kjeller shielded areas, which at reasonable expenses could be used for installation of a semi-industrial irradiation plant.

The maximum activity of the cobalt-60 source is about 120,000 Ci, at present, however, the source strength is 20,000 Ci. Flexibility has been the keyword in the design of the plant, it is primarily intended for development and service in the field of radiation technology, but to some extent it will also be capable of serving Norwegian industry in radiation processing.

Studies on the radiation and catalytical sulfoxidation of alkanes I

The dependence of the sulfoxidation rate on the conversion and the SO_2/O_2-ratio

Bengt Bjellqvist
Department of Nuclear Chemistry
The Royal Institute of Technology, Stockholm Sweden

Summary: It is shown that in purified dry cyclohexane or n-alkane the sulfoxidation reaction starts spontaneously after an induction period. The reaction rates as a function of time have been determined for different mole ratios SO_2/O_2. Initially the reaction rate seems to be growing exponentially. The time-constant increases with the SO_2/O_2-ratio as well as with the total pressure at constant SO_2/O_2-ratio. This result is ascribed to radical production through the reaction

$$RSO_2O_2H + SO_2 \rightarrow RSO_3^{\cdot} + HSO_3^{\cdot}$$

and competition between the reactions

$$R^{\cdot} + SO_2 \rightarrow RSO_2^{\cdot}$$

and

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$$

where the formation of alkylperoxyradicals leads to termination according to

$$RO_2^{\cdot} + \text{radical} \rightarrow \text{stable product}$$

With high gas flows and good mixing the reaction rate reaches a maximum value and then decreases in a manner which indicates inhibition by the products formed. It is shown that addition of sulfuric acid inhibits the reaction. The product inhibition is ascribed to the fact that intermediate species concentrate in the product phase. The sulfonylradical then reacts with either persulfonic acid or sulfonylperoxyradical in the product phase, thus explaining the increased sulfonic acid/sulfuric acid-ratio at high hydrocarbon conversions.

Studies on the radiation and catalytical sulfoxidation of alkanes II

A pulseradiolysis study on the reactions of cyclohexyl-radical with SO_2 and O_2 respectively.

Bengt Bjellqvist and Torbjörn Reitberger
Department of Nuclear Chemistry
The Royal Institute of Technology, Stockholm Sweden

Summary: The transient absorptions produced by pulses of high-energy electrons into pure cyclohexane resp into cyclohexane containing SO_2 or O_2 have been studied. The UV-absorption spectr observed are ascribed to cyclohexyl-, cyclohexylsulfinyl-, resp cyclohexylperoxyradicals. The cyclohexylradical spectrum has a maximum at $\lambda \leq 240$ nm and $\epsilon_{240} = (2,3 \pm 0,7) \cdot 10^3 M^{-1}\ cm^{-1}$. The cyclohexylsulfinyl radical probably has a maximum at $\lambda = 355$ nm with $\epsilon_{355} = 1020 \pm 300\ M^{-1}cm^{-1}$. Contrary to what is earlier reported for the cyclohexylperoxyradical we have found only one absorption maximum with $\lambda_{max} = 255$ nm and $\epsilon_{255} = (4 \pm 1) \cdot 10^3 M^{-1}cm^{-1}$.

The rate-constants for the reactions

$$C_6H_{11}\cdot + SO_2 \xrightarrow{k_1} C_6H_{11}SO_2\cdot \qquad (1)$$

and

$$C_6H_{11}\cdot + O_2 \xrightarrow{k_7} C_6H_{11}O_2\cdot \qquad (7)$$

have been determined to $k_1 = (2,0 \pm 1) \cdot 10^9\ M^{-1}s^{-1}$ and $k_7 = (3,4 \pm 0,6) \cdot 10^9\ M^{-1}s^{-1}$.

The importance of the competition between reactions (1) and (7) for the sulfoxidation in the presence and absence of water is also discussed.

RADIATION INDUCED SPECIES IN DNA AND ITS BASES

by

T. Brustad, H. Bugge and W.B.G. Jones[x]

Norsk Hydro's Institute for Cancer Research, Montebello, Oslo 3, Norway.

I. Time Course of Anoxic Binding of Organic Nitroxyls to Irradiated DNA as Revealed by Disappearance of Nitroxyl Spin and by Formation of ^{3}H-Nitroxyl-DNA Complexes.

(Presented by W.B.G. Jones)

II. Longlived Radiation Induced Free Radicals in Anoxic Wet DNA, as Studied by Electron Spin Resonance.

(Presented by T. Brustad)

III. Second Order Rate Constants for Reactions Between Two Stable Organic Nitroxide Free Radicals and OH-induced Transients in the DNA Bases.

(Presented by H. Bugge)

[x] Fellow in Radiobiological Research of the James Picker Foundation recommended by the Committee on Radiology NAS-NRC.

I. Time Course of Anoxic Binding of Organic Nitroxyls to Irradiated DNA, as Revealed by Disappearance of Nitroxyl Spin and by Formation of ^{3}H-Nitroxyl-DNA Complexes.

(Presented by W. B. G. Jones)

SUMMARY

It has been suggested that the stable free radical N-oxyls such as 2, 2, 6, 6, tetramethyl-4-piperidone-N-oxyl (TAN) may act as cellular radiosensitizers somehow by reacting with OH-induced DNA transients :

$$DNA^{\cdot} + \text{N-oxyl} \longrightarrow [\text{DNA-N-oxyl}] \text{ complex}$$

By application of a rapid mixing technique, with a time resolution of about 10^{-2} sec, unirradiated ^{3}H-TAN (2×10^{-5} M) was mixed with irradiated DNA (1 mg/ml in 10^{2} M NaCl) at predetermined times (t) after irradiation (with 10^{-2} sec $< t <$ 1800 sec). After irradiation and mixing the samples were subjected a) to ESR analysis and b) to analysis by column chromatography.

The former technique enables one to determine the number of remaining free nitroxyl spins after completion of reactions between radiation induced DNA radicals and the nitroxyl radical.

The latter technique permits determination of the fraction of the nitroxyl ^{3}H-activity which becomes covalently bound to radiation induced DNA transients.

The results obtained so far indicate that the time course of the disappearance of free TAN spins follows qualitatively that of the appearance of nitroxyl ^{3}H-activity bound to DNA (at least for times less than 1 sec), showing a rapid component for the reaction between TAN and irradiated DNA which appears to be complete by approximately 350 msec. Details of these time courses will be discussed. Furthermore, from the binding data, some radiation induced

DNA transients appear to be remarkably stable, persisting for times approaching one minute. Under conditions of extremely high DNA concentration, so-called "wet DNA", the radiation induced DNA radicals are even more stable (see presentation II).

II. Longlived Radiation Induced Free Radicals in Anoxic Wet DNA, as Studied by Electron Spin Resonance.

(Presented by T. Brustad)

SUMMARY

A technique is described which permits samples of hydrated anoxic DNA to be exposed at room temperature to a dose of 1 Mrad in less than one second, stored at room temperature for predetermined periods of time, and then frozen at liquid nitrogen temperature. The samples were then analysed at 77 K in an ESR spectrometer.

The experiments show that

a) radiation induced radicals in hydrated DNA are remarkably stable at room temperature. About 10% of those radicals which are detected 9 sec after termination of irradiation persist for more than 2 hours.

b) the number of radicals which persist 5 minutes after termination of irradiation appear to decay according to second order kinetics. Furthermore, the ESR spectrum of these radicals is found to be nearly identical to that for radiation induced powdered thymidylic acid.

c) Preliminary results indicate that immediately after termination of irradiation of the hydrated DNA the contribution to the total radical yield from species differing from those of irradiated powdered thymidylic acid may amount to about 20%.

III.

Second Order Rate Constants for Reactions Between Two Stable Organic Nitroxide Free Radicals and OH-induced Transients in the DNA Bases.

(Presented by H. Bugge)

SUMMARY

Second order rate constants for reactions between some OH-induced transients in cytosine and thymine and the two nitroxyl compounds, 2, 2, 6, 6, tetramethyl-4-piperidone-N-oxyl (also called triacetoneamine-N-oxyl, TAN) and 2, 2, 6, 6, tetramethyl-4-piperidinol-N-oxyl (TMPN) have been determined in 0.02 M phosphate buffer at pH 7, employing pulse radiolysis technique. The results show a marked difference in reactivity between TAN and TMPN. For thymine measured at 400 nm the second order rate constant is found to be $3.2 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TAN and $2.3 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TMPN. For cytosine measured at 425 nm, it is found to be $3.7 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TAN and $3.1 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TMPN. The determination of the rate constants for the reactions between OH-induced transients in adenine with the same nitroxyl compounds has not been successful because of the lower reactivity and OH-scavenging of the nitroxyl compounds; an upper limit of $\sim 10^7 M^{-1}s^{-1}$ is found for adenine at 550 nm.

[illegible] the reactions [illegible] (TMPN) and [illegible] the reactions took place.

ESR Spectra from Paramagnetic Centers in Irradiated $KBrO_4$ Crystals.

J. R. Byberg

Abstract.

ESR spectra of $KBrO_4$ crystals irradiated with x-rays at 10^oK contain "families" of intense signals. Signals observed at 10^oK are assumed to derive from primary defects constituted by electrons and holes trapped on BrO_4^- ions. One family of signals is assigned to the paramagnetic ion $BrO_4^=$ trapped in two inequivalent sites. Another family is assigned to the radical BrO_4 trapped in four inequivalent sites. Thermal processes starting at 22^oK result in formation of the secondary defects O_3^- from $BrO_4^=$ and BrO_2 from BrO_4. These results are analogous to those obtained previously from irradiated $KClO_4$ crystals, which have the same crystal structure as $KBrO_4$. Thus it appears that the ClO_4^- ion and the BrO_4^- ion interact with ionizing radiation in the same way when located in similar crystal fields.

Pulse radiolysis of aqueous solutions of aniline and aniline derivatives.

Hilbert Christensen[x] and S.O. Nielsen[xx]

x) AB Atomenergi, Studsvik, Nyköping, Sweden

xx) Danish AEC Research Establ. Risø, Roskilde, Denmark

Reactions of H atoms with the anilinium ion ϕNH_3^+ and of H atoms and solvated electrons with aniline ϕNH_2 have been studied using either methanol or hydrogen (at a high pressure) as OH scavengers and the spectra of the resulting radicals have been recorded. The results are given in the table, which also contains values for the reaction of OH radicals with aniline and aniline derivatives. The derivatives were studied primarily in order to clarify the aniline system.

Reaction	Rate constant $M^{-1} \cdot s^{-1}$	Radical formed	Absorption maxima with ε within brackets in $M^{-1} \cdot cm^{-1}$
$H + \phi NH_3^+$	$(1.3 \pm 0.2) \cdot 10^9$	$H\phi NH_3^+$	310 (3200)
$H + \phi NH_2$	$(2.9 \pm 0.7) \cdot 10^9$	$H\phi NH_2$	355 (4100)
$e^-_{aq} + \phi NH_2$	$(2.6 \pm 0.3) \cdot 10^7$	$(\phi NH_2)^- \leftrightarrow H\phi NH_2$	355 (4100)
$OH + \phi NH_2$	$(1.4 \pm 0.3) \cdot 10^{10}$	$OH\phi NH_2$ ϕNH_2OH	300 (2300), 400 (1300) 355 (2300)
$O^- + \phi NH_2$	$(3.1 \pm 0.6) \cdot 10^9$	$(O\phi NH_2)^- \leftrightarrow OH\phi NH_2$	300 (2700), 400 (1200)
$OH + \phi NH_3^+$	$(5.0 \pm 0.9) \cdot 10^9$	$OH\phi NH_3^+$	415 (2200)
$OH + \phi N(CH_3)_2$	$1.3 \cdot 10^{10}$	$OH\phi N(CH_3)_2$	328 (3900), 455 (3000)
$OH + \phi N^+H(CH_3)_2$		$OH\phi N^+H(CH_3)_2$	270 (4300), 455 (1500)
$OH + (CH_3)_2\phi NH_2$		$(OH)(CH_3)_2\phi NH_2$ $(CH_3)_2\phi NH_2OH$	295 (3300), 400 (1100) 350 (1400)

The values of the extinction coefficients should be regarded as relative values only, when more than one maximum is present. An H or OH before φ means the formation of a cyclohexadienyl radical.

In unbuffered aniline and 2-amino-1,3-dimethylbenzene solutions two types of radicals were formed due to addition of OH radicals either to the benzene nucleous or to the NH_2-group. In unbuffered N,N'-dimethylaniline (DMA) and in acid aniline and DMA solutions only addition to the nucleous took place.

Experience with the Use of an Industrial 10 MeV Electron Accelerator

Per Dalager og Henning Rindorf
RADEST A/S, Glostrup

Abstract

The great success in the early nineteen-sixties at the accelerator-department of Risø with radiation sterilization of medical utensils made it too difficult for Risø to concentrate on research and at the same time made it attractive for industry to set up a plant for electron-irradiation.

A new company - RADEST A/S - was founded and since spring 1968 the 10 kW, 10 MeV electron accelerator installed at RADEST has rendered irradiation services for Danish Manufacturers.

The paper will give a brief description of the accelerator as well as the accessories, that are very necessary to ensure a trouble-free working of an industrial plant.

The first 1000 days of running the RADEST-plant has shown that irradiation with electrons can be used for a surprisingly wide variety of items and purposes, some of which will be mentioned.

The technical experiences we have gained in the daily work with the accelerator-plant will be discussed in some detail.

Finally an outlook for the future - as we see it - of electron-irradiation will be given.

Paper proposed to the meeting in Nordisk Forening for Strålingsforskning og Strålingsteknologi, 8-9 february 1971.

Abstract

The Influence of Dose Rate on Radiation Inactivation of Str.faecium, strain $A_2$1, and B.sphaericus, strain C_1A.

by

Claus Emborg

Accelerator Department

Radiation sterilization is to-day carried out by two kinds of radiation sources, electron accelerators and gamma sources. The dose rate of an industrial electron accelerator can be up to 1 million times higher than the dose rate of a gamma sterilisation plant.

E.A. Christensen observed several years ago (E.A. Christensen, L O. Kallings, draft to Code of Practice for Radiation Sterilisation of Medical Products, IAEA, Vienna, 1966) that the same dose of radiation, given at different dose rates, does not always have the same inactivating effect on bacteria in dried preparation, high dose rate radiation being less efficient than lower dose rate. These dose rate effects are, however, not found with all strains of bacteria.

Str.faecium, strain $A_2$1, which is applied as the vegetative reference standard for radiation sterilization, is an example of a bacterial strain where a clear dose rate effect can be observed. The radiation resistance as well as the dose rate effect varies with humidity. The dose rate effect is totally absent when irradiated in suspension, has a relative constant magnitude (1o-2o%) at 1o-9o% r.h., but decreases somewhat at extreme drying.

B.sphaericus, strain C_1A, the spore monitor for efficiency of radiation sterilisation is an example of an organism where no dose rate effect has been observed under the conditions so far tested.

[illegible] system so [illegible] light [illegible] through the measuring cell to the signal photo- [illegible] and directly to the photomultiplier which regulates the [illegible] supply.

On the radiation chemistry of S(IV)-oxyacids.

T E Eriksen Johan Lind

Department of Nuclear Chemistry

The Royal Institute of Technology, Stockholm Sweden

Studies of the radiation chemistry of S(IV)-oxyacids are carried out at our department. The systems are complicated, involving a number of species and protolytic equilibria.

UV-spectroscopic methods for product analysis have been developed. These spectra will also be of importance for the pulse radiolysis experiments as small shifts in the above mentioned equilibria will take place.

At the moment γ-radiolysis experiments are carried out.

LONGTIME INTENSITY STABILIZATION OF THE ARC IN A XENON LAMP

J. Fenger and K.B. Hansen

Danish A.E.C. Research Establishment Risø, Roskilde, Denmark

A 450 W xenon lamp is a useful light source in the pulse radiolysis apparatus. The light power is in the wave length region from 200-1200 nm, and short-time stability up to 1 ms is excellent. For measuring periods up to 1 s, however, it has been found that the light intensity might fluctuate as much as 30%. The fluctuations in intensity occur in two ways. One is due to partial intensity variation in the arc itself, and the other one is due to physical wavering of the arc. The latter tending to increase during the lifetime of the lamp.

In the set up for pulse radiolysis experimentation with a 10 MeV electron beam from an accelerator, the light path from the lamp to the monochromator outside the accelerator shielding is around 10 m. Even a small shift in the arc position will give large displacement relative to the monochromator slit position. The enlargement in the present system is four times.

The first step was to try to stabilize the arc by introducing a magnetic field around the arc, the field being regulated by the help of two sensing diodes. However, this method did not sufficiently stabilize the light intensity, even of the small portion of the light arc that was used. The next procedure was to stabilize the light intensity by regulating the lamp current by means of a specially designed current regulator. This could not be accomplished by interfering with the light beam itself. Therefore, the light was stabilized succesful to better than 0.5% by connecting this current regulator directly from the signal photomultiplier at the output of the monochromator.

Finally, after stabilizing the light, we add a chopper system so as to chop the light at 1 kHz. The controlled intermittent light signal then passes both through the measuring cell to the signal photomultiplier and directly to the photomultiplier which regulates the lamp current supply.

RADIATION-INDUCED EMULSION POLYMERIZATION OF VINYL MONOMERS IN A RECYCLE REACTOR SYSTEM AND CHARACTERIZATION OF THE PRODUCTS OBTAINED*

Nils Friis[x], Jørgen Kops[xx] and Klaus Singer[x]

[x] Danish Atomic Energy Commission, Research Establishment Risoe, Chemistry Department, Roskilde, Denmark

[xx] Institutet for Kemiindustri, Technical University of Denmark

Almost all studies concerned with radiation-induced emulsion polymerization have been made in small batch systems with the primary purpose to investigate the kinetics of the reaction, while the properties of the isolated polymers have only been studied to a smaller extent.

In this investigation it is the intention to carry out the emulsion polymerization of vinyl monomers in a recycle reactor system, and to study the relationship between the process parameters and the properties of the isolated polymers. The system consists of a backmix reactor outside a Co^{60}-source, connected by transfer lines to a plug flow reactor positioned within the Co^{60}-source. In the laboratory set-up it is possible continously to measure the rate of polymerization.

The properties of the polymers and the rate of reaction will be determined as functions of flow rate, dose rate, temperature and emulsifier concentration. The properties to be investigated are molecular weight distribution, degree of branching and mechanical strength. First we want to study the emulsion polymerization of vinyl acetate because of its considerable technological importance. Later the investigation will be extended also to include acrylic copolymers.

The lecture will include a more detailed description of the flow reactor system together with an elucidation of some theoretical aspects behind the radiation induced polymerization in such a system.

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* to be presented at the 2nd Scandinavian Radiation Chemistry Meeting, Copenhagen/Risö, February 8-9, 1971

General survey concerning irradiation treatment of food-stuffs in Europe.

Maire Jaarma
Biokemiska institutionen, Stockholms Universitet,
S-113 82 Stockholm, Sweden.

Since the foundation of ESNA (European Society of Nuclear Methods in Agriculture) about one and a half year ago - in Wageningen - several countries in Europe Co-operate through different working groups in this field. A special group is engaged in "Technical Aspects of Food Irradiation" with the aim of international co-operation. The intention of the group is an effort to comply with the desire of the FAO/WHO/IAEA expert committee to obtain a technical background to aid the development of legislation on irradiated food products. Equal decisions in all countries would facilitate the international merchandizing of these food products.

In general the future possibilities for the irradiation treatment of food-stuffs are judged to be very positive - and the chances to obtain permission for irradiation of a number of food products are very good.

For some objects calculations for costs of the irradiation treatment as compared to other preservation methods have been performed.

The existing commercial applications and pilot plants prove that there is a growing belief in the irradiation treatment of food-stuffs.

ESR-study of γ-irradiated benzene and its derivatives in the adsorbed state

Tsuyoshi Komatsu
Forskningsrådens laboratorium,
Studsvik, Fack, S-611 01 Nyköping 1, Sverige

Radiolysis of benzene and its derivatives in the adsorbed state has been studied by ESR method. Inorganic adsorbents such as silica gel, vycor glass and molecular sieves were used.

Heat treatment of silica gel was performed at temperatures of 250 to 750°C for 24 h under an ultimate pressure of 10^{-5} torr. The yields of both benzene radical cations and cyclohexadienyl radical decreased with increasing heating temperature. The fraction of dimer benzene radical cation $\cdot(C_6H_6)_2^+$ increased at higher heating temperatures. These facts are due to a decrease of hydroxyl group concentration on the surface of the silica gel.

The silica gel synthesized from $SiCl_4$ and the gel treated with strong acids gave low yields of the benzene radical cations whereas the yield of the cyclohexadienyl radical was almost unaltered.

The ESR spectrum of γ-irradiated toluene adsorbed on the silica gel showed a very complicated line shape assigned to both the toluene monomer radical cation and dimer radical cation. After warming or illumination with infrared light, only the ESR spectrum of the dimer radical cation was observed. The ESR spectrum of toluene-α-d_3 monomer radical cation consists of 13 lines of about 3 G separation. This spectrum is quite different from that of the undeuterated toluene. The formation of a radical anion seems improbable in the adsorbed state because the significant effect of deuterated methyl group on the hyperfine structure of the ESR spectrum is not expected for a toluene radical anion.

The ESR spectra of the γ-irradiated toluenes adsorbed on the vycor glass are similar to these obtained in the toluene - silica gel system. The ESR spectra of γ-irradiated toluenes adsorbed on molecular sieves are assigned not only to the radical cation, but also to benzyl radical.

Computer assisted spectral analysis of ESR data

Anders Lund
Forskningsrådens laboratorium
Studsvik, Fack, S-611 01 Nyköping 1, Sverige

The analysis of complex spectra containing several superimposed components has been attempted using a computer program called ASESK. The spectrum to be analyzed F(x) is fitted to a relation of the type

$$F(x_i) = \sum_{j=1}^{m} a_j f_j(x_i)$$

at a number of equidistant field points x_i. Here a_j represents the fraction of the component f_j being present. These components may either be simulated by ASESK from given coupling constants, line widths and g-factors, or be read as a numerical line shape, available from experiment. In the latter case the spectrum is collected in the memory of a computer of average transients (CAT) and punched on paper tape which can be directly used in ASESK. Output is the fractions a_j which errors, together with plots of the composed spectrum its components and the spectrum obtained from the least squares fit. In addition one or more of the components $a_j \cdot f_j(x)$ may be subtracted allowing line profiles of weak absorbtions hidden under the main spectrum to be estimated. The procedure has been tested with the spectrum obtained from single crystal decane following γ-irradiation at 195°K.

The two components are due to the radicals (I) - $CH_3\dot{C}H-CH_2$- and (II) - $CH_2-\dot{C}H-CH_2$-, with $a_I : a_{II} = 1{\cdot}7$. The spectrum obtained after subtracting the intense component (I) yields a septet with a splitting of 33.5 G. The program is limited to the case of symmetric lineshapes containing hyperfine structure from I = 1/2 nuclei. The coupling constants must be given as input data. Work is now in progress to obtain refined values of coupling constants, line widths and g-factors by means of a least squares fit of these parameters.

Radiation Dosimetry by means of Dye Precursors

by

William L. McLaughlin[x)]

Accelerator Department
Atomic Energy Commission
Research Establishment Risø
DK-4000 Roskilde - Denmark

Colourless leuco, carbinol, and nitrile dye forms when properly activated become deeply coloured with large doses of ultraviolet or ionizing radiation. By varying the nature of activating host material, the colouration can be made either transient ($\geq$ 5 μsec) or permanent. The stability and efficiency of coloured molecules produced generally increase with the dielectric constant of the matrix material and are determined somewhat by the pH. For example, the radiation produced colour of carbinols or cyanides of triphenylmethane is stable when they are held in a weakly protonated and strongly polar environment. Such solutions are useful dosimeters because the optical density at the maximum of the absorption band increases linearly with radiation dose. The G value does not vary with dose rate, even for very high-intensity, pulsed radiation fields. Since the solutions can be in the form of liquids, gels, or solids, they can be used in a variety of geometries, covering dose ranges from 10^3 to 10^8 rads. As thin films they are particularly useful above 10^5 rads for the examination of high-resolution dose distributions. Spectral response characteristics show similarities to those of certain biological systems.

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x) Visiting scientist from the National Bureau of Standards, Washington D.C.

Electron Irradiation Curing of Unsaturated Polyester - Styrene based Lacquers and Paints.

Hannu Sairanen, Timo Autio and Jorma K. Miettinen
Department of Radiochemistry, University of Helsinki
Finland

Abstract

Experiments on radiation curing of lacquers and paints based on unsaturated polyester - styrene mixtures have been carried out with a 400 KeV 3 mA electron accelerator.

Dose distribution in width and depth in the paint film as well as dose requirement in curing of a number of experimental paints are described. Results with some additives are reported.

Positron Annihilation in Ice and Frozen Aqueous Solutions

O. Mogensen and M. Eldrup
Chemistry Department, Risö

G. Kvajić and M. Milosević-Kvajić
Institute of Nuclear Sciences
Belgrade, Yugoslavia

Abstract

Linear slit angular correlation curves have been obtained at -148°C, -110°C, and -80°C for the [0001], [10$\bar{1}$0] and [11$\bar{2}$0] directions in single crystals of ice. Pronounced side peaks in the curves were observed. They are explained as evidence for the positronium (Ps) center-of-mass wave function being a Bloch function, i.e. positronium is delocalized in ice.

The lifetimes of positrons and positronium in polycrystalline H_2O and D_2O ice, single crystals of H_2O ice, and ice doped with HF and HCl were measured in the temperature interval $0°C \leq t \leq -186°C$. For concentrations above about 10^{-4}M HF or HCl in polycrystalline ice at -160°C the ortho-Ps lifetime increases to 1,2 ns compared to 0.6 ns in pure ice. This is interpreted as trapping of ortho-Ps in holes in the structure (perhaps L-defects) created by the impurities. The corresponding trapping rate constant $k \approx 10^{13}$ l/(mole.sec) is 110 times larger than the largest Ps-quenching rate constant in water (quenching by $Cr_2O_7^{--}$ ions). This is probably due to the Ps-delocalization in ice.

We have also measured angular correlation curves for frozen aqueous solutions of HF, HCl, HBr, HI, $FeCl_2$, $FeCl_3$, NH_3, $K_2Cr_2O_7$, $MnSO_4$, $KMnO_4$, H_2SO_4 and HNO_3 and angular correlation studies of the interaction of positrons with vacancies in aluminium single crystals are in progress.

Computer Simulation of E.S.R. Experiments.

J. Møller

Abstract.

E.S.R. spectra of a large number of paramagnetic point defects in irradiated chlorates, bromates, perchlorates and perbromates show hyperfine structure from one or two nuclei with spin I = 3/2. The E.S.R. spectra may be described in terms of an "effective spin Hamiltonian"

$$\mathcal{H}^S = \beta\bar{B}\cdot\bar{\bar{g}}\cdot\bar{S} + \bar{S}\cdot\bar{\bar{A}}_1\cdot\bar{I}_1 + \bar{S}\cdot\bar{\bar{A}}_2\cdot\bar{I}_2 + \bar{I}_1\cdot\bar{\bar{Q}}_1\cdot\bar{I}_1 + \bar{I}_2\cdot\bar{\bar{Q}}_2\cdot\bar{I}_2 - \gamma_1\bar{B}\cdot\bar{I}_1 - \gamma_2\bar{B}\cdot\bar{I}_2$$

($S = 1/2$, $I_1 = 3/2$, $I_2 = 3/2$).

The experimental job consists of determination of the principal values and the orientation of the principal axes relative to the crystallographic axes for the tensors $\bar{\bar{g}}$, $\bar{\bar{A}}_1$, $\bar{\bar{A}}_2$, $\bar{\bar{Q}}_1$ and $\bar{\bar{Q}}_2$.

To accomplish this, we have developed a method for simulation of the E.S.R. spectrum for a given choice of the parameters in $\mathcal{H}^S(\bar{\bar{g}}, \bar{\bar{A}}_1, \bar{\bar{A}}_2, \bar{\bar{Q}}_1, \bar{\bar{Q}}_2)$ and for any orientation of the static magnetic field $\bar{B}$.

E.S.R. spectra are recorded at fixed microwave frequency by sweeping the magnitude of $\bar{B}$. Accordingly, the E.S.R. experiment is simulated by computing the values of B that make the differences between the energylevels involved in the E.S.R. transitions equal to the incident microwave quanta.

The positions of the E.S.R. transitions on the magnetic field scale may be plotted as a function of the orientation of $\bar{B}$ relative to the crystallographic axes. Also, a single

E.S.R. spectrum may be plotted using a Gaussian or Lorentzian line shape function.

The computations are carried out at N.E.U.C.C., using the IBM 7094 and IBM 360/75 computers.

A sucessful pedagogical experiment involving radiation chemistry, or How to activate the students.

Kerstin Niblaeus Johan Lind T E Eriksen

Department of Nuclear Chemistry

The Royal Institute of Technology, Stockholm Sweden

In order to activate the students in the laborative training in nuclear chemistry, some pedagogical experiments are undertaken.

The students are given a selection of problems in radiation- and nuclear chemistry. The nature of the problems is such that they can not directly be solved by the use of laboratory manuals, text books etc. The students are supposed to attack and solve the problems independently. They have to their disposal a gamma cell, a pulse radiolysis equipment analytical devices etc.

The reaction among the students is very positive and an increasing interest has been noticed so far. Thus this is an experiment where the teaching is closely related to active research with the best equipment available. The experiments will continue in January 1971.

Pulse Radiolytic Measurement of the Rate of Reaction of H with Methanol, Ethanol, and Isopropanol in Aqueous Solution

S.O. Nielsen and Palle Pagsberg
Chemistry Department, Danish Atomic Energy Commission,
Research Establishment Risö, Roskilde, Denmark

and

Hilbert Christensen and Gösta Nilsson
Aktiebolaget Atomenergi, Studsvik, Nyköping, Sverige

To free hydrogen atoms in aqueous solution we have assigned (J. Phys. Chem. 73, 1029 (1969)) a moderately strong light absorption at 200 nm which may be used for monitoring reaction rates of hydrogen atoms. The rates of H + H, H + OH, and H + O_2 had previously been determined in this manner and found to be essentially diffusion controlled. The purpose of the present investigation was to extend these measurements to some non-diffusion controlled reactions of H atoms.

Acid aqueous solutions of alcohols (methanol, ethanol, or isopropanol) were pulse radiolysed and the optical transmission monitored in the range 200-230 nm. Alcohol concentrations were chosen so that OH radicals had reacted almost completely at the end of the electron pulse whereas H atoms reacted at slower rates with half-lives of from 1 to 20 μsec. These rates compete with the rate of reaction of H with itself and with alcohol radicals. At 220 and 230 nm where H atoms make only a small contribution to optical absorption in comparison with the alcohol radicals the results were compatible with the published rate constants of H + H and H + alcohol. The results obtained at 200 nm where H atoms make an appreciable contribution to the measured optical absorption shortly after the pulse show that the disappearance of absorbance due to free H atoms is synchronous with the disappearance of H atoms even when these are removed in non-diffusion controlled reactions with alcohols in agreement with the assignment of a far-ultraviolet spectrum to free H atoms in aqueous solution.

The Kinetics of Transient Electrons in Crystalline Ice.

G Nilsson, H C Christensen,[x)]
P Pagsberg and S O Nielsen.[xx)]

x) AB Atomenergi, Studsvik, Nyköping, Sweden.
xx) Danish Atomic Energy Commission Research Establishment Risø, Roskilde, Denmark.

At present there is no general agreement regarding the reaction order of the electron in crystalline ice. Current models of the electron decay will therefore be discussed and compared with the resultsof our own computer calculations which seems to favour general second order kinetics in H_2O and D_2O-ice in the temperature range 0 - 50°C.

The Reduction of Ferricytochrome C Studied by Pulse Radiolysis

Karen Nilsson, Palle Pagsberg

Department of Chemistry
Danish Atomic Energy Commission,
Research Establishment Risö

Abstract

The kinetics of the reduction of ferricytochrome c to ferrocytochrome c in aqueous solution has been studied by means of pulse radiolysis. Hydrated electrons as well as OH radicals both formed in the radiolysis of water participate in the reduction. Rate constants indicate that hydrated electrons reduce ferricytochrome c directly whereas the reduction of cytochrome c by OH radicals may be by a secondary process. The nature of the secondary process will be discussed.

Paper withdrawn

Pulse Radiolysis of Aqueous solutions of Hydrazine.

P.B. Pagsberg[1] and J.W. Sutherland[2]

Hydrazine is readily oxidised by OH radicals in aqueous solution. The net reaction is a decomposition into nitrogen and ammonia. The mechanism involves three unstable intermediates:

$$N_2H_4 + OH \longrightarrow N_2H_3 + H_2O \qquad (1)$$

$$2\ N_2H_3 \longrightarrow N_4H_6 \qquad (2)$$

$$N_4H_6 \longrightarrow N_3H_3 + NH_3 \qquad (3)$$

$$N_3H_3 \longrightarrow N_2 + NH_3 \qquad (4)$$

The absorption spectra of N_2H_3 and N_3H_3 are very similar in shape, and both are centered at 230 nm. However the extinction coefficients are different, 2750 $M^{-1}cm^{-1}$ for N_2H_3 and about twice for N_3H_3. This seems to imply a triplet state of N_3H_3 rather than the double bond structure, which should give rise to an absorption at about 250 nm characteristic to the N=N chromophore. The bimolecular rate constants are $k_1 = 3.7 \times 10^9\ M^{-1}s^{-1}$ and $2k_2 = 1.8 \times 10^9\ M^{-1}s^{-1}$. The first order rate constants k_3 and k_4 show a strong dependence of pH, indicating acid and base catalysis. The minimum values are $k_3 = 20\ s^{-1}$ at pH = 11.7 and $k_4 = 0.04\ s^{-1}$ at pH = 8.3.

1) Danish A.E.C. Research Establishment Risø, Roskilde, Denmark.

2) Brookhaven National Laboratory, Upton, N.Y., U.S.A.

ON DELAYED EFFECTS IN THE RADIOLYSIS OF AQUEOUS PROTEIN SOLUTIONS.

Kai O. Pedersen

Institute of Physical Chemistry, University of Uppsala,
Box 532, S-751 21 Uppsala 1.

Electrolyte-free aqueous solutions of monomer bovine serum albumin have been irradiated under various experimental conditions in the gamma-cells at Studsvik and at Risö as well as in the linear accelerator at Risö. After the irradiation the solutions have been frozen and in this condition transferred to Uppsala where they were stored at -15° C until further study could be carried out. The main effect of the irradiation was the formation of dimers and higher polymers of the albumin molecule; some splitting might also be observed. After thawing, and in case of the dilute solutions also concentrating, the solutions were fractionated on Sephadex columns whereby the amount of "monomer" and the various polymers was determined.

When aliquots from the frozen solutions were studied at intervals of 10 to 20 months, a gradual increase of the highest polymer was always found to have taken place during these periods at the sacrifice of the lower polymers and of the monomer. The effect was more pronounced in the dilute solutions (0.15 and 0.025 percent albumin) than in the most concentrated ones (5 percent). This "after-effect" could be hastened by keeping the irradiated solutions at 40° C for 10 to 20 hours prior to fractionation on Sephadex columns. The very dilute solutions should preferably be concentrated to 1 to 2 percent before warming. Effects similar to those found after warming to 40° C could also be obtained by a final strong concentration (at room temperature) of the dilute solutions up to 5 to 10 percent.

The "after-effect" is also manifested in the spectrum of the irradiated solutions where, after heating to 40° C, a marked increase took place in the light absorption, especially around 300 mμ.

RADIOLYSIS OF AQUEOUS SOLUTIONS OF SOME SIMPLE COMPOUNDS CONTAINING ALDEHYDE GROUPS

PART II: GLYOXYLIC ACID

K. Sehested and V. Marković

The reaction mechanism in aqueous solution of glyoxylic acid was investigated by pulse radiolysis and product determinations. The experiments were done at different dose rates, concentrations and pH.

Both radicals H and OH react preferably with the aldehyde group in glyoxylic acid forming the radical $C(OH)_2COOH$ by H abstraction. The dose rate and the concentration of the solute are important because of the competition between second order radical-radical recombination and pseudo-first order radical-solute reaction. The rate constant for the first order reaction was found to be of the order of $10^5 \cdot M^{-1} \cdot sec^{-1}$. The product of this reaction is the radical CHOHCOOH also formed directly in the radiolysis of glycollic acid. The absorption spectra and decay kinetics of the two radicals differ significantly.

The products from the recombination of the two radicals are dihydroxytartaric acid and tartaric acid respectively.

ESR-studies of 1,3-butadiene adsorbed on silica gel. I. The evidence for the formation of 1,3-butadiene cation radical.

Tetsuo Shiga, Forskningsrådens laboratorium, Studsvik, Fack, S-611 01 Nyköping 1, Sverige.

The adsorbed system is useful to stabilize reactive intermediate species formed by ionizing radiation. Silica gel is one of the useful and interesting adsorbent, because either anionic, cationic and neutral radicals are produced according to the nature of adsorbates and the interaction with the silica gel.

It is of interest to investigate what kinds of radical are produced by γ-irradiation from 1,3-butadiene adsorbed on silica gel, since butadiene polymerizes with catalysts of either radical, cationic or anionic type.

Butadiene was dried by passing it through a column packed with the molecular sieve 3A and 4A, previously baked under the pressure of 10^{-5} torr. Silica gel was dried at 600 C for 24h under the pressure of 10^{-5} torr. 0,1 mole % of butadiene was irradiated at 77°K with total dose of 0.8 Mrad.

The spectrum at 77°K is composed of a septet separated by about 15 G superimposed on the signal with a hyperfine splitting less than 15 G. At 195°K the signal with the smaller hyperfine splitting disappears. The decaying spectrum exhibits a quintet of lines separated by about 11 G. In the presence of 0.8 mole % of triethylamine the quintet separated by 11 G are not formed. Triethylamine has high proton affinity and lower ionizatinn potential than butadiene. Then it can work as either a proton scavenger or a positive charge scavenger. Therefore the quintet is indicated to be associated with a cationic species.

The calculation of hyperfine coupling constants of butadiene cation radical from spin density and charge density gives the value of $a_1 = a_4 = 11.4$ G and $a_2 = a_3 = 3.2$ G. The quintet agrees quite well with the computed spectrum using these coupling constants. Therefore it is assigned to 1,3-butadiene cation radical.

The spectrum from 0.2 % of 1,3-butadiene-1,1,4,4-$\underline{d}_4$ gives further support to the butadiene cation formation.

Butadiene cation initiates the cationic polymerisation at butadiene concentration about 3 % and higher.

Hot Atom Chemistry of ^{82}Br in bromobenzenes

K.E. Siekierska and J. Fenger
Chemistry Department, Danish
Atomic Energy Commission,
Research Establishment Risö

Radiogaschromatography shows that after neutron irradiation of each of the seven *mono-*, di- and tri bromobenzenes about 25% of the total ^{82}Br activity is in inorganic form, about 17% in the form of the parent bromobenzene and a few % in the form of other bromobenzenes (preferably addition products). This, however, accounts for only about half of the total activity; the rest is found in the inlet system and has not been conclusively identified. It is solvent and concentration dependent and its behaviour indicates that it contains at least two, probably heavy, species: one which can be hydrolyzed and one which resists hydrolysis. The nature and mechanism of formation of these species is discussed with reference to radiolytical phenomena observed in monobromobenzene.

ABSTRACT

Growth of irradiated spores of Clostridium botulinum 62A in synthetic media.

B.G. Snygg

Swedish Institute for Food Preservation Research, Göteborg

Irradiated and unirradiated spores of Clostridium botulinum 62A were subcultured in various synthetic agar media and in thiotone agar. The thiotone medium gave higher colony counts of unirradiated spores than did the synthetic media. When the spores had been irradiated some of the synthetic media gave the highest spore counts.

The spore crops were grown in a trypticase medium, harvested after 4 to 5 days incubation at 37C, lysozyme-trypsin treated and washed in distilled water. The spore suspensions were irradiated in distilled water in polypropylene tubes at +5C. The maximum dose was 1.0 Mrad reached in 0.1 or 0.25 Mrad increments. After irradiation the spores were plated in deep tube cultures. The maximum counts were reached after 2 days in thiotone or 4 days in the synthetic media when incubated at 37C.

The original synthetic medium contained the compounds listed below.

L-arginine	17.2 mM	L-tyrosine	1.4 mM
L-isoleucine	3.8 mM	DL-valine	17.1 mM
L-leucine	11.4 mM	glucose	13.9 mM
L-methionine	4.0 mM	$NaHCO_3$	14.9 mM
L-phenylalanine	12.1 mM	biotin	0.0005 µg/ml
L-threonine	8.4 mM	p-aminobensoesyra	0.01 -"-
L-tryptophan	0.25mM	thiamine	0.4 -"-

This medium supported poor growth of both irradiated and unirradiated spores. When supplemented with e.g. L-alanine 4.5 mM, L-cysteine 7.4 mM, L-histidine 1.3 mM and L-lysine 8.2 mM or L-alanine, L-cysteine, L-histidine, L-proline 4.3 mM and L-serine 9.5 mM these media gave slightly lower or the same counts of unirradiated spores but about twice as many survivors at 0.5 Mrad and 5 times as many at 0.8 Mrad as the thiotone medium. When the growth rate was slowed down by incubation at lower temperatures the surviving fraction decreased in synthetic media as well as in thiotone.

On the chemical fate of hot ^{11}C atoms in water and aqueous solutions

by Tore Stenström, The Gustaf Werner Institute, University of Uppsala and Department of Radiobiology, The Agricultural College of Sweden, S 750 07 Uppsala 7, Sweden.

Abstract

The chemical fate of ^{11}C atoms induced by nuclear reactions in proton-irradiated water and aqueous solutions was studied. The results are interpreted in terms of (1) hot reactions leading to primary ^{11}C products, assumed to be single-carbon molecules or radicals with yields independent of solutes at low concentrations, and (2) thermal reactions, in which the primary products react in the bulk of the solution with radiation-induced radicals or, in the case of ^{11}C radicals, with a solute to give the observed ^{11}C end products.

In carefully purified deaerated water, radiation-induced oxidation of primary products yielded $^{11}CO_2$ as the only important product at high doses. By use of radical scavengers the molecular ^{11}C products could, however, be largely protected from radical attack and in oxygenated solutions primary ^{11}C radicals were oxidized in an unequivocal way.

The following yields of primary ^{11}C products were thus determined: $^{11}CO_2$+$^{11}COOH$ = 9±3%; ^{11}CO = 44.5±1%; $H^{11}COOH$+$H^{11}C(OH)_2$ = 16±1%; $H^{11}CHO$+$^{11}CH_2OH$ = 26%±2%; $^{11}CH_3OH$+$^{11}CH_3$ = 4±1%; $^{11}CH_4$ = 0.06±0.02%.

In deaerated aqueous solutions, the reactions were found to be more complicated and ^{11}C radicals were oxidized or reduced, or combined with organic solute radicals to give products containing more than one carbon atom. From the experimental results in different dilute solutions an attempt was made to determine the yields of primary ^{11}C molecules and radicals separately. Due to incomplete knowledge of the radical reactions, the following yield data of primary products are only tentative: $^{11}CO_2$ = 6%, $^{11}COOH$ = 3%, ^{11}CO = 44.5%, $H^{11}COOH$ = 8%, $H^{11}C(OH)_2$ = 8%, $H^{11}CHO$ = 18%, $^{11}CH_2OH$ = 6%, $^{11}CH_3OH$ = 4%, $^{11}CH_3$ = 0.2%, and $^{11}CH_4$ = 0.06%.

A few experiments were made with concentrated aqueous solutions to elucidate the hot reactions leading to the above products. It was shown, for example, that the yield of $^{11}CO_2$ was decreased to about 1% in the presence of 1.1M potassium iodide or 2M ethanol. The yield of $H^{11}COOH$ was also considerably decreased. Hot reactions between nascent ^{11}C atoms and water are discussed on the basis of these experiments and results in non-aqueous systems studied by other workers. The following reactions appear to be important: (1) reactions with a lone electron pair giving ^{11}CO, and (2) insertion of ^{11}C into an O-H bond giving H-^{11}C-OH which may fragment or react further to give $H^{11}CHO$, and (3) reactions involving ^{11}C intermediate fragments such as ^{11}CH, ^{11}COH, $^{11}CH_2$, and $^{11}C(OH)_2$.

This work was published by the author in a more complete form as a thesis with the title: "On the chemical fate of nascent ^{11}C atoms induced by irradiation of water and aqueous solutions with 185 MeV protons", Uppsala, Sweden, 1970.

ESR Spectra of Radicals Produced by UV Photolysis of Cystine Dihydrochloride Single Crystals

E. Lund Thomsen

Chemistry Department, Danish Atomic Energy Commission, Research Establishment Risö

The esr spectra of single crystals of cystine dihydrochloride, irradiated at room temperature with monochromatic u.v. light at various wavelengths has been measured. Two thiyl radicals are observed: The thiyl radical first observed by Kurita and Gordy that is formed by γ-irradiation of the crystals and another thiyl radical with g-values approx. equal to the g-values of the first mentioned radical but with a different orientation in the crystal lattice. Some observations regarding the mechanism of formation will by presented.

Presentation by O. Vinther.

Defect centers induced in single crystals of $NaClO_3$ by low temperature irradiation.

by

O. Vinther
Institute of Chemistry
University of Århus
Denmark

Defects generated in single crystals of $NaClO_3$ at low temperature by ionizing radiation has been studied using ESR- and UV-spectroscopy. Centers detected after irradiation at -247^0 C are ClO_3(A), ClO_2, O^{2-} and possibly $(ClO_3)_2^-$. Irradiation at -196^0 C produces in addition another modification of ClO_3(B), which differs from the original one with respect to orientation relative to the crystallographic axis of the host crystal. The two modifications are assumed to be related by inversion through the center of the unit cell.

The ClO_3(B)-center can be transformed into the ClO_3(A)-center by illumination of the crystal with light of wavelengths greather than 5500Å. The ClO_3-centers are thermally unstable above -180^0 C and decay probably due to an interaction with O^{2-}. Illumination with visibel light into the absorption-band of O^{2-} makes the disappearence of ClO_3(B)-centers proceed rapidly, whereas the ClO_3(A)-center is not affected. A possible explanation to this difference in behaviour of the two ClO_3-centers will be discussed.

Oxidation of CH_3SH and H_2S with ozone.

Björn Widén T E Eriksen Johan Lind

Department of Nuclear Chemistry

The Royal Institute of Technology, Stockholm Sweden

A study has been initiated with the object to learn the *mechanisms of radiation oxidation of hydrogen sulfide*, mercaptans etc, a thing of basic, geochemical and environmental interest. The latter point of course refers to the kraft mill off gases in the wood-industry. The study presented here deals with the more easy study of oxidation with a radiomimetic gas, namely ozone.

An air stream, 1,5 l/min, containing 0,5 - 1% ozone (vol) reacted with a low flow of methylmercaptan, 350 mmol/min in a 500 ml flask. Gas samples were taken with a gas tight syringe and analyzed gaschromatographically. (Varian Aerograph 1520, FiD, column: 25 % TCP on Varaport 30; 70°C; 25 ml/min N_2).

97 - 98 % of the mercaptan reacted according to the chromatograms. 45 % was oxidized to methylsulfonic acid and the corresponding anhydride. Other identified products were dimethyldisulfide and formaldehyde. 60 % of hydrogen sulfide reacted under similar conditions with sulfurdioxide as the main product. (EC-detector).

RADIATION INDUCED SPECIES IN DNA AND ITS BASES

by

T. Brustad, H. Bugge and W. E. G. Jones*

Norsk Hydro's Institute for Cancer Research, Montebello, Oslo 3, Norway.

I. Time Course of Anoxic Binding of Organic Nitroxyls to Irradiated DNA as Revealed by Disappearance of Nitroxyl Spin and by Formation of ^{3}H-Nitroxyl-DNA Complexes.

(Presented by W. B. G. Jones)

II. Longlived Radiation Induced Free Radicals in Anoxic Wet DNA, as Studied by Electron Spin Resonance.

(Presented by T. Brustad)

III. Second Order Rate Constants for Reactions Between Two Stable Organic Nitroxide Free Radicals and OH-induced Transients in the DNA Bases.

(Presented by H. Bugge)

*Fellow in Radiobiological Research of the James Picker Foundation recommended by the Committee on Radiology NAS-NRC.

I. Time Course of Anoxic Binding of Organic Nitroxyls to Irradiated DNA, as Revealed by Disappearance of Nitroxyl Spin and by Formation of ^{3}H-Nitroxyl-DNA Complexes.

(Presented by W. B. G. Jones)

SUMMARY

It has been suggested that the stable free radical N-oxyls such as 2, 2, 6, 6, tetramethyl-4-piperidone-N-oxyl (TAN) may act as cellular radiosensitizers somehow by reacting with OH-induced DNA transients :

$$DNA^{*} + \text{N-oxyl} \longrightarrow [\text{DNA-N-oxyl}] \text{ complex}$$

By application of a rapid mixing technique, with a time resolution of about 10^{-2} sec, unirradiated ^{3}H-TAN (2×10^{-5} M) was mixed with irradiated DNA (1 mg/ml in 10^{2} M NaCl) at predetermined times (t) after irradiation (with 10^{-2} sec $< t <$ 1800 sec). After irradiation and mixing the samples were subjected a) to ESR analysis and b) to analysis by column chromatography.

The former technique enables one to determine the number of remaining free nitroxyl spins after completion of reactions between radiation induced DNA radicals and the nitroxyl radical.

The latter technique permits determination of the fraction of the nitroxyl ^{3}H-activity which becomes covalently bound to radiation induced DNA transients.

The results obtained so far indicate that the time course of the disappearance of free TAN spins follows qualitatively that of the appearance of nitroxyl ^{3}H-activity bound to DNA (at least for times less than 1 sec), showing a rapid component for the reaction between TAN and irradiated DNA which appears to be complete by approximately 350 msec. Details of these time courses will be discussed. Furthermore, from the binding data, some radiation induced

DNA transients appear to be remarkably stable, persisting for times approaching one minute. Under conditions of extremely high DNA concentration, so-called "wet DNA", the radiation induced DNA radicals are even more stable (see presentation II).

II. Longlived Radiation Induced Free Radicals in Anoxic Wet DNA, as Studied by Electron Spin Resonance.

(Presented by T. Brustad)

SUMMARY

A technique is described which permits samples of hydrated anoxic DNA to be exposed at room temperature to a dose of 1 Mrad in less than one second, stored at room temperature for predetermined periods of time, and then frozen at liquid nitrogen temperature. The samples were then analyzed at 77 K in an ESR spectrometer.

The experiments show that

a) radiation induced radicals in hydrated DNA are remarkably stable at room temperature. About 10% of those radicals which are detected 9 sec after termination of irradiation persist for more than 2 hours.

b) the number of radicals which persist 5 minutes after termination of irradiation appear to decay according to second order kinetics. Furthermore, the ESR spectrum of these radicals is found to be nearly identical to that for radiation induced powdered thymidylic acid.

c) Preliminary results indicate that immediately after termination of irradiation of the hydrated DNA the contribution to the total radical yield from species differing from those of irradiated powdered thymidylic acid may amount to about 20%.

III.

Second Order Rate Constants for Reactions Between Two Stable Organic Nitroxide Free Radicals and OH-induced Transients in the DNA Bases.

(Presented by H. Bugge)

SUMMARY

Second order rate constants for reactions between some OH-induced transients in cytosine and thymine and the two nitroxyl compounds, 2,2,6,6, tetramethyl-4-piperidone-N-oxyl (also called triacetoneamine-N-oxyl, TAN) and 2,2,6,6, tetramethyl-4-piperidinol-N-oxyl (TMPN) have been determined in 0.02 M phosphate buffer at pH 7, employing pulse radiolysis technique. The results show a marked difference in reactivity between TAN and TMPN. For thymine measured at 400 nm the second order rate constant is found to be $3.2 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TAN and $2.3 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TMPN. For cytosine measured at 425 nm, it is found to be $3.7 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TAN and $3.1 \pm 0.1\ 10^8 M^{-1}s^{-1}$ with TMPN. The determination of the rate constants for the reactions between OH-induced transients in adenine with the same nitroxyl compounds has not been successful because of the lower reactivity and OH-scavenging of the nitroxyl compounds; an upper limit of $\sim 10^7 M^{-1}s^{-1}$ is found for adenine at 550 nm.

INTRODUCTION

The observation that anoxic or hypoxic regions appear in certain malignant tumours has led to an intensive search for drugs which preferentially sensitize anoxic cells (1). Thus, considerable attention has been drawn to the radiosensitizing effects of certain organic nitroxide free radicals. To shed more light on the mechanisms of action of these compounds it has been found appropriate to study reactions between these free radicals and some OH-induced

transients in the DNA bases. These studies will be reported on here. The nitroxide radicals concerned in the present investigation are the 2,2,6,6, tetramethyl-4-piperidone-N-oxyl (also called triacetoneamine-N-oxyl, TAN) and the related compound 2,2,6,6, tetramethyl-4-piperidinol-N-oxyl (TMPN). Similar studies of the reaction between TAN and the OH-adduct of thymine, which absorbs at 400 nm has been performed earlier by Emmerson and Willson (2).

EXPERIMENTAL SECTION

All experiments were carried out in 0.02 M phosphate buffer at pH 7 to make the conditions somewhat comparable to those of biological systems. Triple distilled water was used throughout. DNA bases of the highest purity commercially available were obtained from Fluka AG, Basel and used without further purification. The nitroxyl compounds were synthesized in this department by Dr. W.B.G. Jones. Nitrous oxide was obtained from Norgas A/S, Oslo, and made oxygen-free by bubbling through strongly alkaline pyrogallol. The test-solutions were bubbled with N_2O for about 40 minutes before irradiation.

The experimental setup, described elsewhere (3,4) is built up around a 4 MeV linac. The light path through the sample cuvette was 2 cm. Two Bausch & Lomb grating monochromators were used. The dose was measured by means of the KCNS system (5) after each experiment. Radiation doses ranging from 2 to 4 krad were used. For adenine, however, doses up to 15 krad were applied. All oscillograms were converted to optical density as a function of time by means of a Wang tabletop computer with attached curve-reading equipment and then plotted. The decay constants were calculated by exponential regression analysis (6) (assuming the decays to follow pseudo first order kinetics). Solutions of the nitroxyls saturated with N_2O were

irradiated, and no radiation induced absorbance was found at the wavelengths concerned in this work.

Thymine.

The radiation induced absorption peak at 400 nm was chosen for measurement. This is the same wavelength as that used by Emmerson and Willson in their work (2).

Fig. 1 and b illustrates the effect of TMPN on the decay of the thymine transients.

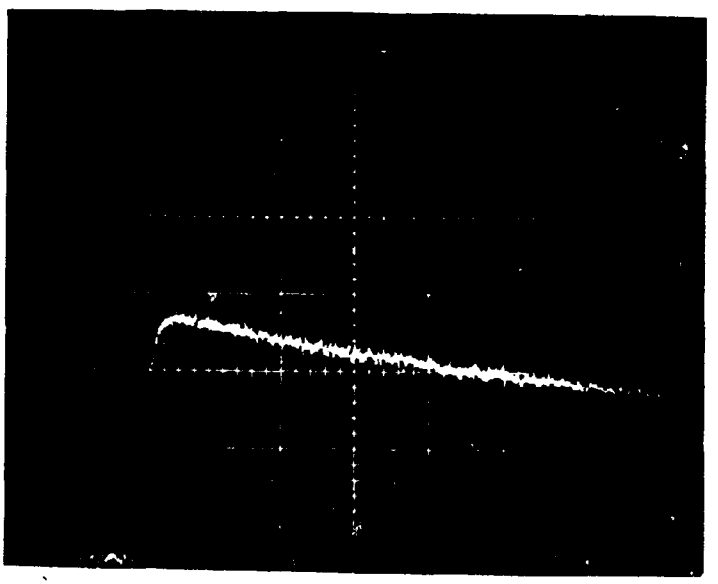

Fig. 1 a.

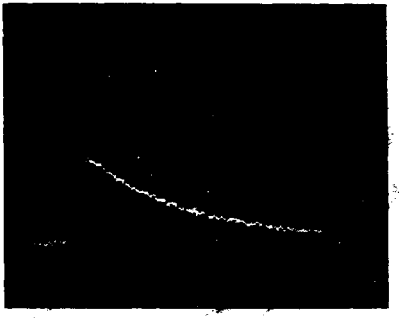

Fig. 1 b.

Fig. 1. Pulse radiolysis trace of a) solution of $5 \cdot 10^{-4}$M thymine in 0.02 M phosphate buffer, pH 7, N_2O-saturated.
b) solution of $5 \cdot 10^{-4}$M thymine/$3 \cdot 10^{-4}$M TMPN in 0.02 M phosphate buffer, pH 7, N_2O-saturated.
Both pictures : abscissa 5 μs/div and ordinate 2% abs/div. Dose approximately 3.5 krad. Reduction in absorption in Fig. 1 b, relative to that in Fig. 1 a, is due to nitroxyl scavenging of radicals.

Solutions of $5 \cdot 10^{-4}$M thymine were irradiated in presence of various concentrations of TMPN, oxygen-free and N_2O-saturated. An example of the decay patterns obtained is shown in Fig. 2.

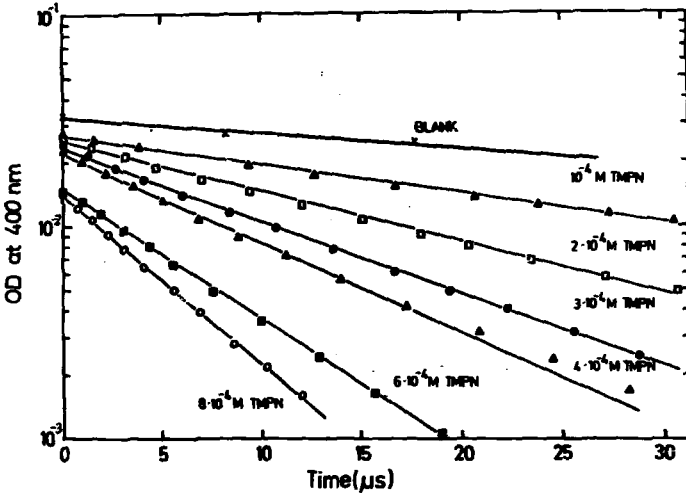

Fig. 2. Decay patterns obtained for a $5 \cdot 10^{-4}$M thymine solution in 0.02 M phosphate buffer, pH 7, at 400 nm, in presence of various concentrations of TMPN. The points are seen to fit straight lines.

The corresponding rate constants are shown in Fig. 3, indicating a pseudo first order reaction scheme. This clearly demonstrates that TMPN reacts similarly to TAN (2), the second order rate constant for thymine OH adduct + TMPN is found to be $(2,3 \pm 0,1)\ 10^{8} M^{-1} s^{-1}$.

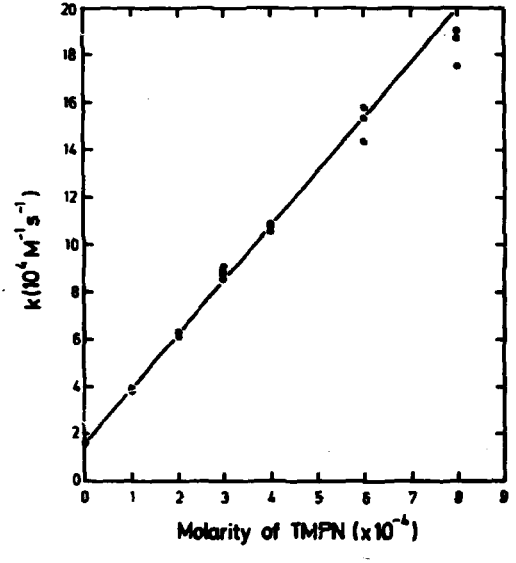

Fig. 3. Rate constants for the reaction between thymine OH˙ adduct at 400 nm and TMPN. Each point represents one oscillogram. The points demonstrate a linear relationship between the decay constants and the TMPN concentration. This is in agreement with pseudo first order kinetics.

We also performed similar studies with TAN, and thus repeated Emmerson and Willson's work (except that we used pH = 7.0) and found $(3.2 \pm 0.1) 10^8 M^{-1} s^{-1}$, which is a somewhat lower value than that obtained by Emmerson and Willson $(3.5 \cdot 10^8 M^{-1} s^{-1})$.

Cytosine.

The absorption peak at 425 nm was chosen for measurement on the basis of spectra taken in N_2O saturated solutions and deaerated solutions containing 10^{-2}M $NaNO_3$, which indicated this peak to be $OH^{\cdot}$ induced. This is in agreement with results published by Myers et al. (7).

Solutions of $5 \cdot 10^{-4}$ M cytosine were irradiated in presence of various concentrations of TMPN, oxygen-free and N_2O-saturated. The second order rate constant was determined as described above and found to be $(3.1 \pm 0.1)\ 10^8 M^{-1} s^{-1}$. The same experiment was performed with TAN which, like the corresponding work with thymine, gave a higher value $(3.7 \pm 0.1)\ 10^8 M^{-1} s^{-1}$.

Adenine.

The stable radiation induced products in adenine solutions were found to give rise to a pronounced absorption, of the same magnitude as that of the radiation induced transients, over most of the wavelength region studied. This made a kinetic investigation more difficult and uncertain. It was found, however, that at 550 nm the contribution to the absorption from stable products was negligible, but the transient absorption itself was also relatively small (compared with that at 300-400 nm). Comparisons between spectra of adenine solutions saturated with N_2O or deaerated solutions containing 10^{-2}M $NaNO_3$ indicated this absorption to be caused by $OH^{\cdot}$ induced transients. Solutions of $5 \cdot 10^{-4}$ M adenine were irradiated in presence of TMPN up to $6 \cdot 10^{-3}$M without any significant reduction of the lifetime of the transient. At this TMPN

concentration the OH scavenging by TMPN (as well as the competition between TMPN and N_2O for e^-_{aq}) makes the absorbance of the adenine transient very small even when the dose is raised to 15 krad, which is close to the maximum dose delivered in one pulse with our setup. It is impossible to increase the concentration of the adenine transients by raising the adenine concentration, as the latter already is close to saturation. However, an upper limit for the rate constant can be estimated to $10^7 M^{-1}s^{-1}$. The same conclusion holds true for TAN. Similar experiments on guanine are also in progress.

CONCLUSIONS

The results here presented demonstrate a marked difference between TAN and TMPN as regards their reactivity towards $OH^\cdot$ induced transients in the DNA pyrimidines. The reactivity of TAN is 20-40% higher than that for TMPN under the present experimental conditions. As regards the radiation induced transients studied in the pyrimidine bases, it seems that the cytosine transient is more reactive than the thymine transient.

Assuming the absorbance at 550 nm in adenine to be caused by $OH^\cdot$ induced transients, which is strongly indicated by absorption spectra taken, the conclusion may be drawn that the reactivity of the DNA purine transients are probably an order of magnitude lower than that of the DNA pyrimidine transients towards TAN and TMPN. Further investigation on the purine transients is, however, needed to support this conclusion.

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